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(54) FORMING METHOD OF PLATING-SUBSTITUTE CONDUCTIVE METAL FILM USING METAL FINE PARTICLE DISPERSED LIQUID

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a method of forming simply and in high reproducibility a conductive metal film which can be substituted for various plating films for various uses in an electronic component material field having process accuracy and reliability comparable to a plating film.
SOLUTION: Extra-fine metal particles with average particle diameter of 100 nm or less are dispersed in an organic solvent with coating layer of an amine compound or the like capable of coordinate bonding with metal element, a coating film is formed with the use of paste-like dispersion liquid with the addition of organic acid anhydride or its derivative or organic acid or the like showing reactivity with the amine compound or the like of the coating layer, and then, is put under heat treatment at 250°C or less, to manufacture a metal film with metal extra-fine particles densely sintered.

CLAIMS

[Claim(s)]
[Claim 1]A method of forming a plating substitution conductive metal coat using metal particulate dispersion liquid, comprising:

A process of forming a coating layer of said metal particulate dispersion liquid in a field which forms a plating substitution conducting film.
Heat-treat a coating layer of said formed metal particulate dispersion liquid at temperature which does not exceed 250 **, have the process of sintering both the metal particles to contain, and said metal particulate dispersion liquid to be used, They are nitrogen, oxygen, and a sulfur atom as a basis in which a metallic element by which an ultra-fine particle chosen as a range whose mean particle diameter is 1-100 nm is distributed in an organic solvent used as a carrier fluid object, and the ultra-fine particle surface is included in this ultra-fine particle and coordination combination are possible.

[Claim 2]In temperature which performs said heat-treatment to said compound which has a basis which contains nitrogen, oxygen, and a sulfur atom in metal particulate dispersion liquid as a basis which has covered the ultra-fine particle surface, and in which a metallic element and coordination combination are possible, Dissociation of said compound which the nitrogen, oxygen, a basis containing a sulfur atom, and a compound which has reactivity are dissolved, and has nitrogen from the ultra-fine particle surface, oxygen, and a basis containing a sulfur atom, A method according to claim 1 being promoted by reaction of the nitrogen, oxygen and a basis containing a sulfur atom to said compound which has this nitrogen, oxygen, and a basis containing a sulfur atom, and said compound which has reactivity.
[Claim 3]A method of using an organic acid anhydride, its derivative, or organic acid as said nitrogen, oxygen, a basis containing a sulfur atom, and a compound which has reactivity which are contained in metal particulate dispersion liquid according to claim 2.
[Claim 4]Said ultra-fine particle contained in metal particulate dispersion liquid, Gold, silver, copper, platinum, palladium, tungsten, nickel, tantalum, A method of being particles which consist of one kind of metal chosen from a group which consists of bismuth, lead, indium, tin, zinc, titanium, and aluminum, or the particles of an alloy which consists of two or more kinds of metal according to claim 1 or 2.
[Claim 5]Are metal particulate dispersion liquid used for formation of a plating substitution conducting film, and said metal particulate dispersion liquid, An ultra-fine particle chosen as a range whose mean particle diameter is 1-100 nm is distributed in an organic solvent used as a carrier fluid object, and the ultra-fine particle surface, As a basis in which a metallic element contained in this ultra-fine particle and coordination combination are possible, It is covered with one or more sorts of compounds which have nitrogen, oxygen, and a basis containing a sulfur atom, and as a basis in which a metallic element and coordination combination are possible, Metal particulate dispersion liquid characterized by the ability to dissociate from the ultra-fine particle surface by heat-treatment at temperature to which said compound which has nitrogen, oxygen, and a basis containing a sulfur atom does not exceed 250 **.
[Claim 6]In temperature which performs said heat-treatment to said compound which has a basis which contains nitrogen, oxygen, and a sulfur atom in metal particulate dispersion liquid as a basis which has covered the ultra-fine particle surface, and in which a metallic element and coordination combination are possible, The metal particulate dispersion liquid according to claim 5, wherein the nitrogen, oxygen, a basis containing a sulfur atom, and a compound which has reactivity are dissolved.
[Claim 7]The metal particulate dispersion liquid according to claim 6, wherein said

nitrogen, oxygen and a basis containing a sulfur atom which are contained in metal particulate dispersion liquid, and a compound which has reactivity are an organic acid anhydride, its derivative, or organic acid.
[Claim 8]Said ultra-fine particle contained in metal particulate dispersion liquid, Gold, silver, copper, platinum, palladium, tungsten, nickel, tantalum, Particles which consist of one kind of metal chosen from a group which consists of bismuth, lead, indium, tin, zinc, titanium, and aluminum, or the metal particulate dispersion liquid according to claim 5 or 6 being the particles of an alloy which consists of two or more kinds of metal.
[Claim 9]Are the method of carrying electronic parts on a substrate, and said electronic parts, As opposed to a wiring circuit where a flow is achieved via a conductive metal coat and which is formed on a substrate, A loading method of electronic parts, wherein said conductive metal coat which has a process carried so that electric connection may be taken, and is formed on a substrate is formed by a method indicated to either of claims 1-4.
[Claim 10]A method according to claim 9, wherein a conductive metal coat which aims at a flow is an alternative conductive metal film of a plating film for through holes between the surface of a substrate, and a rear face.
[Claim 11]A method according to claim 9, wherein a conductive metal coat which aims at a flow is an alternative conductive metal film of a plating film which constitutes at least a part of wiring circuit currently formed on a substrate.
[Claim 12]A method according to claim 9, wherein a conductive metal coat which aims at a flow is an alternative conductive metal film of a plating film for bonding in which connection with a wiring circuit and wiring of electronic parts which are formed on a substrate is made.
DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention about the formation method of the conductive metal coat for plating substitution more specifically, Using metal particulate dispersion liquid, the coating film of the formed metal particulate dispersion liquid is heat-treated, both the metal particles to contain are sintered, and it is related with the method of forming the conductive metal coat for plating substitution, and the metal particulate dispersion liquid used for it. This invention relates also to the method of carrying electronic parts on a substrate using the conductive metal coat for plating substitution which replaces with various conductive members formed by the conventional plating, and is formed by the aforementioned method.
[0002]
[Description of the Prior Art]In the electronic industry material field, the plating film is used for various uses and proper use of the electroplating method or the electroless deposition method is made according to the use. The uses of plating in the electronic industry material field include plating for through holes, plating for etching resist, plating for terminals, plating for bonding, plating for electric contact, plating for soldering, plating for adhesion, etc., for example. In a multilayer interconnection board, plating for through holes in which a metallic film which carries out the following, respectively is formed with plating according to these uses is plating to the through hole in which a

substrate is penetrated and formed in order to plan electrical continuity between layers. A copper thin film is used for the wiring circuit by the side of the surface and the rear face where a flow is generally achieved via this through hole, it corresponds and non-electrolytic copper plating is used for plating for through holes. When manufacturing a multilayer interconnection board, the technique of also aiming at the flow of a through hole wall and a flow with the wiring on a substrate, and thickness performing ** attachment radio solution coppering processing of 1 micrometer or less beforehand, then performing 10-50-micrometer-thick non-electrolytic copper plating is generally used.
[0003]In a copper through hole wiring board etc., plating for soldering The sake antioxidizing on the surface of copper interconnect, and on a soldering disposition, A wiring board is beforehand immersed into the fused solder, and excessive solder is blown away, and a thin solder layer is covered only on the copper interconnect surface, and it is formed in it as a coating coat for this solder layer protection. Generally, an unelectrolyzed tinning film is used. art, such as the super solder method which look like [the copper interconnect surface] the coating coat of a thin solder layer and its surface with heating after applying organic acid **** and tin powder as a technique formed simultaneously in recent years, and carries out the precoat of the solder, is developed.
[0004]Plating for etching resist is used to etching resist, such as a dry film and liquid resist, and, generally gold plate was used for in the past. In recent years, a solder plate becomes in use, in addition tinning is also used.
[0005]Plating for terminals is plating to the terminal surface which performs a connector and an electrical link.
By low resistance, after ground plating gold plate, palladium plating, rhodium plating, etc. which show good corrosion resistance and abrasion resistance, it is formed and used. On the other hand, as for this ground plating, a nickel plate, a palladium nickel plate, nickel boron electroless nickel plating, etc. are used.
[0006]In the wiring board which has electric contact, such as a keyboard, in a circuit, plating for electric contact is plating performed to the electric contact.
After all, a nickel plate is considered as ground plating and the gold plate formed on it is used.

[0007]Plating for bonding is plating performed to the copper surface of wiring, in order that the copper used for the base of wiring may prevent expressing by diffusion, when performing bonding.
Gold plate of the high grade excellent in bonding nature is used.

[0008]Plating for adhesion is used for adhesive improvement with inner package copper foil and prepreg in the case of formation of multilayer lamination. Usually, although oxidation treatment of a copper surface is performed for adhesive improvement with prepreg, in order to prevent invading the copper oxide to generate, non-electrolytic copper plating and unelectrolyzed tinning are given to the surface.
[0009]In the electronic industry material field, when forming the metallic film which has various uses, stable junction is possible, and since it has good workability and high mass production nature, generally the formation method of the metallic film by plating treatment is used from before, so that it may mention above. However, in the use described above, when performing plating treatment, such as gold, silver, copper,

palladium, and nickel, to the field made into the purpose selectively, before performing the plating, the process of performing pretreatment to a ground is needed. In a actual plating process, after using for plating treatment in connection with using the solution of a cyanogen system for a plating bath, the waste liquid treatment of these cyanogen system solution is needed. To make doubly sure, in waste liquid treatment, although cyanide ion is detoxified by oxidation etc., use of strong toxic medicine, such as a cyanogen system compound, is gradually kept at arm's length from the consideration to peripheral environment.

[0010]

[Problem(s) to be Solved by the Invention]In the electronic industry material field, so that it may mention above plating, It has the essential technical problem that it is generated by a considerable quantity of waste fluid which should process various metallic films in connection with use of the cyanogen system solution described above, and a subsequent washing process by a wet type although used in the wide range as a means producible with high reproducibility. It gropes for replacing a part of process where plating was conventionally used using the means producible with high reproducibility in various metallic films, avoiding this technical problem.

[0011]This invention solves the aforementioned technical problem and the purpose of this invention, In the electronic industry material field, for example, junction to electronic parts, circuit drawing on a wiring board, It is in providing the method of replacing with various plating used for each use, such as flow formation in a through hole etc., and having the process tolerance and reliability which are equal to the metallic film and the plating film for which it can be substituted by these plating, and forming a conductive metal coat with high reproducibility by a simple process. The purpose of this invention more specifically uses the metal particulate dispersion liquid which consists of target metal, It is in forming this metal particulate dispersion liquid coating film in a desired field, sintering both the metal particles that heat-treat and contain this coating film, and providing the method of forming the conductive metal coat for plating substitution, and the metal particulate dispersion liquid used for it.

[0012]

[Means for Solving the Problem]If this invention persons produce a coating film of metal particles and make both the particles contained in a coating film of this metal particle sinter after that that the above-mentioned technical problem should be solved when they advance research and examination wholeheartedly, It thought out for forming a metallic film which has homogeneity and conductivity comparable as a plating film to be possible. When attaining process tolerance comparable as a plating film, It is necessary to consider it as a very fine thing without detailed metal-particles size which constitutes a metallic film produced by plating in mean particle diameter of metal particles to be used, and inferiority, In addition, it found out that it was necessary for such very detailed metal particles to produce a coating film made into a precise filling state, and to attain sintering at low temperature in comparison by the state further. The first requirements are satisfied by using an ultra-fine particle chosen as a range whose mean particle diameter is 1-100 nm as metal particles to be used according to process tolerance among these three requirements, and also about the last requirements. When it was made to contact mutually after there is no oxide layer in that surface and a metal atom has exposed this ultra-fine particle, it found out that it was possible to make it sinter easily by heat-treating at

temperature of 250 ** or less, for example. However, about the second requirement said ultra-fine particle, If it is made to contact mutually where it is exposed of a metal atom on the surface, as a result of adhesion (weld) arising mutually and causing aggregate formation sparse in comparison also at temperature near a room temperature, it found out that it was also difficult to attain a precise filling state without a plating film and inferiority with high reproducibility as a whole. When examination is further advanced in order to find out a solving means of this technical problem, on the metal atom surface of an ultra-fine particle as a basis in which a metallic element contained in this ultra-fine particle and coordination combination are possible, Aggregate formation is avoidable if it changes into the state where it was covered with one or more sorts of compounds which have nitrogen, oxygen, and a basis containing a sulfur atom, When an organic solvent which it is possible to make it distribute uniformly, and forms a coating film of these dispersion liquid, and is contained in an organic solvent was transpired, it found out that it was possible to change into the state where it filled up with an ultra-fine particle precisely. At temperature which heat-treats in an organic solvent, as a basis in which a metallic element and coordination combination are possible, If the nitrogen, oxygen, a basis containing a sulfur atom, and a compound which has reactivity are dissolved to said compound which has nitrogen, oxygen, and a basis containing a sulfur atom, A reaction of said compound which has a basis which contains nitrogen, oxygen, and a sulfur atom which dissociate gradually also thermally in the case of heating, and a compound which has the reactivity to it advances, As a result, the metal atom itself expressed on the surface of an ultra-fine particle, both these surfaces of metal were enabled to carry out direct contact, sintering took place also by processing at comparison low temperature, and it found out that a metallic film of a precise sinter molding object could be formed. This invention persons came to complete this invention based on knowledge of these series.

[0013]Namely, a formation method of a plating substitution conductive metal film of this invention, A process of forming a coating layer of said metal particulate dispersion liquid in a field which is the method of forming a plating substitution conductive metal coat, and forms a plating substitution conducting film using metal particulate dispersion liquid, Heat-treat a coating layer of said formed metal particulate dispersion liquid at temperature which does not exceed 250 **, have the process of sintering both the metal particles to contain, and said metal particulate dispersion liquid to be used, An ultra-fine particle chosen as a range whose mean particle diameter is 1-100 nm is distributed in an organic solvent used as a carrier fluid object, and the ultra-fine particle surface, As a basis in which a metallic element contained in this ultra-fine particle and coordination combination are possible, When it is covered with one or more sorts of compounds which have nitrogen, oxygen, and a basis containing a sulfur atom and said heat-treatment is performed, as a basis in which a metallic element and coordination combination are possible, It is a formation method of a plating substitution conductive metal film, wherein dissociation from the ultra-fine particle surface of said compound which has nitrogen, oxygen, and a basis containing a sulfur atom is made.

[0014]In a formation method of a plating substitution conductive metal film of this this invention, In temperature which performs said heat-treatment to said compound which has a basis which contains nitrogen, oxygen, and a sulfur atom in metal particulate dispersion liquid to be used as a basis which has covered the ultra-fine particle surface,

and in which a metallic element and coordination combination are possible, Dissociation of said compound which the nitrogen, oxygen, a basis containing a sulfur atom, and a compound which has reactivity are dissolved, and has nitrogen from the ultra-fine particle surface, oxygen, and a basis containing a sulfur atom, It is preferred to consider it as a method being promoted by reaction of the nitrogen, oxygen and a basis containing a sulfur atom to said compound which has this nitrogen, oxygen, and a basis containing a sulfur atom, and said compound which has reactivity. In that case, it is preferred to use an organic acid anhydride, its derivative, or organic acid as said nitrogen, oxygen, a basis containing a sulfur atom, and a compound which has reactivity which are contained in metal particulate dispersion liquid.

[0015]On the other hand, a formation method of a plating substitution conductive metal film of this invention, According to construction material of a plating film which should aim at the substitution, said ultra-fine particle contained in metal particulate dispersion liquid, Gold, silver, copper, platinum, palladium, tungsten, nickel, tantalum, It can be considered as a method of being particles which consist of one kind of metal chosen from a group which consists of bismuth, lead, indium, tin, zinc, titanium, and aluminum, or the particles of an alloy which consists of two or more kinds of metal.

[0016]This invention is what also provides collectively an invention of metal particulate dispersion liquid used for a formation method of a plating substitution conductive metal film which has above-mentioned composition, Namely, metal particulate dispersion liquid of this invention is metal particulate dispersion liquid used for formation of a plating substitution conducting film, and said metal particulate dispersion liquid, An ultra-fine particle chosen as a range whose mean particle diameter is 1-100 nm is distributed in an organic solvent used as a carrier fluid object, and the ultra-fine particle surface, As a basis in which a metallic element contained in this ultra-fine particle and coordination combination are possible, It is covered with one or more sorts of compounds which have nitrogen, oxygen, and a basis containing a sulfur atom, and as a basis in which a metallic element and coordination combination are possible, Said compound which has nitrogen, oxygen, and a basis containing a sulfur atom is metal particulate dispersion liquid characterized by the ability to dissociate from the ultra-fine particle surface by heat-treatment at temperature which does not exceed 250 **.

[0017]In metal particulate dispersion liquid of this invention, in the metal particulate dispersion liquid, In temperature which performs said heat-treatment to a metallic element which has covered the ultra-fine particle surface, and said compound which has nitrogen, oxygen, and a basis containing a sulfur atom as a basis in which coordination combination is possible, It is preferred to consider it as metal particulate dispersion liquid, wherein the nitrogen, oxygen, a basis containing a sulfur atom, and a compound which has reactivity are dissolved. As for said nitrogen, oxygen and a basis containing a sulfur atom which are contained in metal particulate dispersion liquid, and a compound which has reactivity, in that case, it is preferred that it is an organic acid anhydride, its derivative, or organic acid.

[0018]On the other hand with metal particulate dispersion liquid of this invention, said ultra-fine particle contained in metal particulate dispersion liquid according to construction material of a plating film which should aim at the substitution, Gold, silver, copper, platinum, palladium, tungsten, nickel, tantalum, It can be considered as metal particulate dispersion liquid being particles which consist of one kind of metal chosen

from a group which consists of bismuth, lead, indium, tin, zinc, titanium, and aluminum, or the particles of an alloy which consists of two or more kinds of metal.
[0019]In addition, this invention as a actual usage pattern of a formation method of a plating substitution conductive metal film of this invention mentioned above, Utilize this plating substitution conductive metal film, provide an invention of process which carries electronic parts on a substrate, and namely, a loading method of electronic parts of this invention, Are the method of carrying electronic parts on a substrate, and said electronic parts, As opposed to a wiring circuit where a flow is achieved via a conductive metal coat and which is formed on a substrate, It is the loading method of electronic parts, wherein said conductive metal coat which has a process carried so that electric connection may be taken, and is formed on a substrate is formed by a formation method of a plating substitution conductive metal film of this invention which has one of the composition mentioned above.
[0020]A conductive metal coat in which a loading method of electronic parts of this invention aims at a flow, for example can be made into a method of being an alternative conductive metal film of a plating film for through holes between the surface of a substrate, and a rear face. A conductive metal coat which aims at a flow can be made into a method of being an alternative conductive metal film of a plating film which constitutes at least a part of wiring circuit currently formed on a substrate. A conductive metal coat which aims at a flow can also be made into a method of being an alternative conductive metal film of a plating film for bonding in which connection with a wiring circuit and wiring of electronic parts which are formed on a substrate is made.
[0021]
[Embodiment of the Invention]Below, the paste state metal particulate dispersion liquid used in that case is explained to details more as the formation method of the plating substitution conductive metal film of this invention.
[0022]In the member for which the metallic film formed with the conventional plating is used, the main use of the formation method of the plating substitution conductive metal film of this invention is substitution by the sintered compact coat of the metal particles comparatively sintered and produced at low temperature as the metallic film in the electronic industry material field. Therefore, as for the sintered compact coat of the metal particles used itself, it is desirable that it is a sintered compact coat of the metal particles which have mean particle diameter comparable as the deposited metal grain size in the plating film for which it should substitute. Therefore, the mean particle diameter is chosen as the range of 1-100 nm according to the target thickness in the plating film for which the ultra-fine particle contained in the paste state metal particulate dispersion liquid to be used should substitute. Preferably, mean particle diameter is chosen as the range of 2-10 nm.
[0023]generally boiling markedly the mean particle diameter of several nanometers - the ultra-fine particle of about 10 nm of numbers rather than the melting point, and sintering at a low temperature (for example, if it is silver 200 **) is known. In a metaled ultrafine particle this low temperature sintering, It is because it originates in this surface diffusion and extension of the interface between particles is made, as a result of the rate of occupying in the whole high atom of the energy state which exists in a particle surface becoming large and becoming so large that surface diffusion of a metal atom cannot ignore, if that particle diameter is fully made small, and sintering is performed. On the

other hand, also [near the room temperature], if surface [of an ultra-fine particle / both] carries out direct contact of this character, it will produce the phenomenon of forming floc. The aforementioned aggregate formation becomes a factor which spoils the homogeneous improved effect of thickness attained as a result of very detailed metal particles' forming a dense filling state. If the structure which formed floc selectively beforehand mixes the effect of having attained desired conductivity, as a whole by forming a dense filling state, it will become a cause it becomes impossible to attain a dense filling state with high reproducibility.

[0024]So, the metal particulate dispersion liquid used for the formation method of the plating substitution conductive metal film of this invention, When forming the coating film of paste state metal particulate dispersion liquid on the surface of the subject of a printed-circuit board etc., In order to prevent the aggregate formation of the metal particles contained in dispersion liquid and to maintain a uniform dispersion state, the surface of an ultra-fine particle is changed into the state where it was covered with the metallic element contained in this ultra-fine particle, and one or more sorts of compounds which have nitrogen, oxygen, and a basis containing a sulfur atom as a basis in which coordination combination is possible. The surface of metal of an ultra-fine particle by namely, the thing changed into the state where it covered densely with the metallic element contained in this ultra-fine particle, and one or more sorts of compounds which have nitrogen, oxygen, and a basis containing a sulfur atom as a basis in which coordination combination is possible. An ultra-fine particle changes into the state where the surface of metal does not carry out direct contact mutually until it performs heat-treatment, after forming a coating film. When applying temporarily by providing this enveloping layer, even if it touches oxygen, the oxide film is also in the state where it is not formed substantially, on the surface of the ultra-fine particle.

[0025]When the compound used for covering of this surface forms a metallic element and coordination combination, nitrogen, oxygen, and the basis that has a lone-pair electrons on a sulfur atom are used, and an amino group is mentioned, for example as a basis containing a nitrogen atom. As a basis containing a sulfur atom, a sulfanil group (-SH) and a sulfide type sulfanediyl group (-S-) are mentioned. As a basis containing an oxygen atom, a hydroxy group and an ether type oxy group (-O-) are mentioned.

[0026]Alkylamine can be mentioned as a representative of the compound which has an available amino group. It is in the state in which a metallic element and coordination combination were formed, that from which it is not desorbed in the usual storage environment and the range which does not specifically amount to 40 ** is preferred for this alkylamine, and its boiling point is [the range of not less than 60 ** and the thing which will be not less than 100 ** preferably] preferred. However, when performing sintering and alloying, it is required for seceding from the surface promptly to be possible, and the range whose boiling point does not exceed 300 **, and the thing which usually serves as the range of 250 ** or less are preferred at least. For example, as alkylamine, C4-C20 are used, the alkyl group is chosen as the range of C8-C18 still more preferably, and what has an amino group at the end of an alkyl chain is used. For example, it is used suitably [that it is easy to maintain and control in the range of a request of content, and it has it when alkylamine of said range of C8-C18 has thermal stability and also keeps the steam pressure at a room temperature etc. so highly etc.] from the field of handling nature. Generally, when forming this coordination

combination, a primary amine type thing shows a higher binding affinity, and is preferred, but a secondary-amine type and a tertiary-amine type compound are also available. Compounds in which two or more approaching amino groups participate in combination, such as a 1,2-diamine type and a 1,3-diamine type, are also available.
[0027]An alkane thiol can be mentioned as a representative of the compound which has an available sulfanil group (-SH). What is not specifically desorbed from this alkane thiol in the usual storage environment and the range which does not amount to 40 ** where a metallic element and coordination combination are formed is preferred, and the range of not less than 60 ** and the thing which will be not less than 100 ** preferably have the preferred boiling point. However, when performing sintering and alloying, it is required for seceding from the surface promptly to be possible, and the range whose boiling point does not exceed 300 **, and the thing which usually serves as the range of 250 ** or less are preferred at least. For example, as an alkane thiol, C4-C20 are used, the alkyl group is chosen as the range of C8-C18 still more preferably, and what has a sulfanil group (-SH) at the end of an alkyl chain is used. For example, the alkane thiol of said range of C8-C18 is used suitably [that maintaining and controlling is easy for the range of a request of content, and it has it etc.] from the field of handling nature, when there is thermal stability and the steam pressure is also kept at a room temperature etc. so highly. Although the thing of a first-class thiol form shows a higher binding affinity and is generally preferred, the compound of the second class thiol form and the third class thiol form is also available. What participates in combination has two or more available sulfanil groups (-SH), such as 1 and 2-dithiol type.
[0028]Alkanediol can be mentioned as a representative of the compound which has an available hydroxy group. That from which it is not desorbed in the usual storage environment and the range which does not specifically amount to 40 ** where a metallic element and coordination combination are formed is preferred, and the range of not less than 60 ** and the thing which usually serves as the range of 100 ** or less have [this alkanediol] the preferred boiling point. However, when performing sintering and alloying, it is required for seceding from the surface promptly to be possible, and the range whose boiling point does not exceed 300 **, and the thing which usually serves as the range of 250 ** or less are preferred at least. For example, what participates in combination has two or more more suitably available hydroxy groups, such as a 1,2-diol type.
[0029]In addition, as a basis in which the metallic element which has covered the surface of an ultra-fine particle mentioned above and coordination combination are possible, When it heats to the compound which has nitrogen, oxygen, and a basis containing a sulfur atom, the nitrogen, oxygen and the compound ingredient that has reactivity with the basis containing a sulfur atom, for example, an organic acid anhydride, an acid anhydride derivative, or organic acid can be added in ultra-fine particle dispersion liquid. When it heats, the compound which has reactivity with the basis containing this nitrogen, oxygen, and a sulfur atom is used in order to remove the adhesion layer with a metallic element and the compound which has nitrogen, oxygen, and a basis containing a sulfur atom as a basis in which coordination combination is possible which covers the surface of an ultra-fine particle mentioned above. Namely, in the ultra-fine particle surface the basis which contains said nitrogen, oxygen, and a sulfur atom after the reaction as a result of reacting to nitrogen in the covering compound which forms the adhesion layer near a

room temperature, oxygen, and the basis containing a sulfur atom with heating, It becomes difficult to form a surface metal atom and coordination combination, and removal is made as a result. This removing function is not exhibited near [where coating film formation of paste state metal particulate dispersion liquid is made] the room temperature, but is exhibited for the first time in the process of heat-treatment over a coating film after that.

[0030]The acid anhydride or acid anhydride derivative added reacts to the compound which has said nitrogen, oxygen, and a basis containing a sulfur atom, for example, an amine compound, thiol compounds, a diol compound, etc. with heating, and specifically, it is used in order to form amide, thioester, and ester. If this amide, thioester, and ester are formed, it will become difficult to form a metal atom and coordination combination, and removal of the surface coated layer of an ultra-fine particle will be made as a result. Therefore, it is distributing uniformly from the first, and the organic solvent contained in a coating film following on transpiring, and taking a precise filling state, direct contact of the surface of metal is carried out, heat-treatment progresses, and a very detailed ultra-fine particle is mutually sintered also at low temperature in comparison. Even if the whole ultra-fine particle in a coating film serves as a precise sintered compact coat eventually and it compares with a plating film, the degree of precision is equal. Therefore, the content of this acid anhydride or an acid anhydride derivative is preferred when it adds exceeding the quantity which becomes an equivalent amount with it at least according to total of the terminal amino group contained in the above-mentioned amine compound, thiol compounds, a diol compound, etc., a sulfanil group (-SH), and a hydroxy group. When an acid anhydride or an acid anhydride derivative is heated, it reacts also to the coat of the metallic oxide which has basicity depending on the case, and since it also has a function which generates metal salt of carboxylic acid, a little superfluous quantity is chosen suitably, also taking the reactivity into consideration.

[0031]As long as the aforementioned reactivity is shown, in particular the acid anhydride, its derivative, or organic acid of the organicity used is not limited. As available organic acid, for example, formic acid, acetic acid, propionic acid, butanoic acid, The straight chain or the branched saturated carboxylic acid of C1-C10, such as hexanoic acid and octylic acid, And acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, benzoic acid, Unsaturated carboxylic acid, such as sorbic acid, and oxalic acid, malonic acid, Dibasic acid, such as sebacic acid, maleic acid, fumaric acid, and itaconic acid etc., In addition to various carboxylic acid, the organic acid of others which replace with a carboxyl group and have a phosphate group (-O-P (O) and $(OH)_2$) or a sulfonic group (-SO_3H), such as phosphoric ester and sulfonic acid, can be mentioned.

[0032]As a derivative of the organic acid anhydride or acid anhydride which can be used suitably, Phthalic anhydride, trimellitic anhydride, pyromellitic dianhydride, anhydrous benzophenone tetracarboxylic acid, Aromatic acid anhydrides, such as ethyleneglycol bis(anhydrotrimellitate) and glycerol tris (anhydrotrimellitate), A maleic anhydride, a succinic anhydride, tetrahydro phthalic anhydride, methyl cyclohexene-dicarboxylic anhydride, Anhydrous methyl NAJIKKU acid, an alkenyl succinic anhydride, hexahydro phthalic anhydride, Aliphatic acid anhydrides, such as annular aliphatic acid anhydrides, such as methylhexahydrophthalic anhydride and a methylcyclohexene tetracarboxylic anhydride, a polyadipic acid anhydride, a poly azelain acid anhydride, and a polysebacic acid anhydride, can be mentioned. Also in this, methyl cyclohexene-dicarboxylic

anhydride, methylhexahydrophthalic anhydride, and these derivatives, it is suitably used from the thing which this invention makes the purpose and for which it is comparatively alike and has moderate reactivity to the terminal amino group of an amine compound, etc. also at a low heat-treatment (sintering) temperature, for example.
[0033]In the formation method of the plating substitution conductive metal film of this invention, although the paste state metal particulate dispersion liquid to be used heat-treated after spreading, when [that] applying, it should contain more than an organic solvent kind as a dispersing solvent which distributes the ultra-fine particle which provided the enveloping layer of the molecule in said surface. It is preferred to change into the state where the above-mentioned nitrogen, oxygen and the compound ingredient that has reactivity with the basis containing a sulfur atom, for example, an organic acid anhydride, an acid anhydride derivative, or organic acid dissolved uniformly into this organic solvent. On the other hand, also while keeping paste state metal particulate dispersion liquid over a long period of time, when the ultra-fine particle which provided the enveloping layer of the molecule in the surface maintains a uniform dispersion state, The organic solvent which is not eluted in the adhesion layer of compounds which have covered the surface of the ultra-fine particle to be used, such as an amine compound, is used suitably.
[0034]Although the thing of a different kind can also be used for the organic solvent used for two sorts of these use and purposes, it is preferred to use the same organic solvent. As long as it can use for two sorts of aforementioned uses, the kind is not limited, but. Solubility, such as the compound which forms the adhesion layer on the surface of an ultra-fine particle, for example, alkylamine etc., is too high, and it is preferred to choose not the solvent that has the high polarity that the adhesion layer on the surface of an ultra-fine particle disappears but a nonpolar solvent, or a low polar solvent.
[0035]In addition, at the temperature which heat-treats at the formation method of the plating substitution conductive metal film of this invention for sintering after spreading, it is preferred to have thermal stability to such an extent that this organic solvent can transpire comparatively promptly and does not cause a pyrolysis etc. in the meantime. When forming a detailed line, in order to apply with screen printing etc. in the process of the spreading as a coating film of the thickness which considers metal particulate dispersion liquid as a request, it is also necessary to maintain in the suitable liquid viscosity range. . If the field of the handling nature is taken into consideration, near a room temperature, will not transpire easily. A nonpolar solvent or a low polar solvent high boiling point [in comparison], for example, a terpineol, A mineral spirit, xylene, toluene, ethylbenzene, mesitylene, etc. can use suitably, and hexane, heptane, octane, Deccan, a dodecane, cyclohexane, cyclooctane, etc. can be used further.
[0036]Therefore, the content of this organic solvent is chosen as the quantity of the compound which has reactivity with the basis containing nitrogen, oxygen, and the sulfur atom which it should dissolve, for example, an organic acid anhydride, its derivative, or organic acid. A content ratio is chosen according to the quantity of the ultra-fine particle distributed, and its dispersion density. In that case, it is usually preferred among paste state metal particulate dispersion liquid to choose the content of per ultra-fine particle 100 mass part of the quality of carrier fluid and said organic solvent as the range of five to 100 mass part. It is necessary to prepare the liquid viscosity of paste state metal particulate dispersion liquid for example, and the addition of an organic solvent is

adjusted according to the controllability of proper spreading performance, for example, line width accuracy, and thickness, It is desirable the range of 1 - 500 Pa-s and to choose the last liquid viscosity as the range of 2 - 200 Pa-s preferably.
[0037]On the other hand, the ultra-fine particle of detailed mean particle diameter contained in paste state metal particulate dispersion liquid, According to the use of the plating film for which the conductive metal film which should be formed substitutes, and its construction material, For example, silver, copper, platinum, palladium, tungsten, nickel, tantalum, The particles which consist of one kind of metal chosen from the group which consists of bismuth, lead, indium, tin, zinc, titanium, and aluminum, or the particles of the alloy which consists of two or more kinds of metal can be chosen suitably. In the usual purpose, the particles which consist of metal which is excellent in the electrical conductivity of itself, such as gold, silver, copper, and platinum, are used in many cases. When using alloy particles and usually using what has the melting point of this alloy higher than the heat-treatment temperature for sintering, the effect of this invention is demonstrated.
[0038]The loading method of the electronic parts of this invention is newly using for the electronic industry material member using a plating film conventionally the conductive metal film which adopts the formation method of the plating substitution conductive metal film mentioned above, and is produced, and is a method of performing mounting and loading of the electronic parts to the mounting board top. In the member for loading of electronic parts, although various plating films are used, It is a range from which heat-treatment of the low-temperature-sintering process of an ultra-fine particle which is a characteristic and indispensable process in the formation method of the plating substitution conductive metal film of this invention does not produce a certain fault unlike the usual plating among them, and substitution of a plating film is possible. The gestalt with which the advantage of not needing the wet process using an aquosity reagent is especially demonstrated in the formation method of the plating substitution conductive metal film of this invention unlike plating is more preferred.
[0039]For example, it is suitable by the case where it requires forming an alternative conductive metal film only in a specific field. Therefore, a series of processes of carrying electronic parts on a substrate, As opposed to the wiring circuit where a flow is achieved via a conductive metal coat in electronic parts and which is formed on the substrate, Although the process carried so that electric connection may be taken is included, in that case, the conductive metal coat currently formed on the substrate is using the formation method of the plating substitution conductive metal film of this invention, and becomes what has a desirable case where it is selectively formed only in a necessary part.
[0040]When the conductive metal coat which aims at a flow is used as an example as an alternative conductive metal film of the plating film for through holes between the surface of a substrate, and a rear face, the case where it is used as an alternative conductive metal film of the plating film which constitutes at least a part of wiring circuit currently formed on the substrate is mentioned. In addition, the case where the conductive metal coat which aims at a flow is used as an alternative conductive metal film of the plating film for bonding in which connection with the wiring circuit and the wiring of electronic parts which are formed on the substrate is made is also mentioned as an example. Electronic parts, such as a chip, are carried in the coating film portion after applying the paste state metal particulate dispersion liquid of this invention to a substrate,

and the low temperature of 250 ** or less ** also enables it to join reliable electronic parts by carrying out heating sintering.
[0041]In addition, in the loading method of the electronic parts of this invention, For the electric flow, and shaping and the solidification between metal particles, the paste state metal particulate dispersion liquid to be used. It is also possible to consider it as the gestalt which mounts two or more electronic parts to this conductive metal film unlike the conductive metal paste which did not use an organic binder but uses the organic binder, using a solder agent further.
[0042]
[Example]Below an example is shown and this invention is more concretely explained to it. Although this example is an example of the best embodiment of this invention, this invention does not receive limitation according to this example.
[0043](Example 1) the ultrafine particle dispersion liquid (trade name: independent part excess disbursement particle perfect silver and Vacuum metallurgy) of the silver marketed -- specifically, The dispersion liquid of the paste state silver ultrafine particle were prepared using the dispersion liquid of a silver particulate with a mean particle diameter of 8 nm which contains dodecyl amine 15 mass part as silver particulate 100 mass part and alkylamine, and contains terpineol 75 mass part as an organic solvent.
[0044]As an acid anhydride used as the ingredient to which paste state silver ultrafine particle dispersion liquid react to the dispersion liquid of said silver particulate with per silver particulate 100 mass part in the dispersion liquid, and react to dodecyl amine at the time of heating, Methylhexahydrophthalic anhydride (Me-HHPA) 10 mass part was added, it fully stirred by stirring deaerator, and equalization was attained. The liquid viscosity of the prepared paste state silver ultrafine particle dispersion liquid is 60 Pa-s.
[0045]The prepared paste state silver ultrafine particle dispersion liquid were applied on the copper-foil face of a copper-clad laminate sheet, golden wiring of the semiconductor part was placed on the coating film of this 80-micrometer thickness, and it heat-treated by the temperature conditions for +210 **x 60 minutes under the inert atmosphere for 150 **x 30 minutes. By this heat-treatment, sintering of the silver ultrafine particle contained in a coating film was made, and immobilization and an electric flow were formed via the sintered compact film of the silver ultrafine particle formed as an alternative layer of the plating film for bonding between the copper-foil face of a copper-clad laminate sheet, and golden wiring of a semiconductor part. The connection resistance value between the golden wiring by which bonding was carried out, and a laminate sheet (copper-foil face) was 1.2×10^{-6}omega at that time.
[0046](Example 2) Paste state silver ultrafine particle dispersion liquid were prepared like Example 1. Per silver particulate 100 mass part with a mean particle diameter of 8 nm and as alkylamine, The dispersion liquid containing terpineol 75 mass part are used as dodecyl amine 15 mass part and an organic solvent, As an acid anhydride used as the ingredient which reacts to the dodecyl amine to contain per silver particulate 100 mass part in the dispersion liquid at the time of heating, methylhexahydrophthalic anhydride (Me-HHPA) 10 mass part was added, it fully stirred by stirring deaerator, and equalization was attained. The liquid viscosity of the prepared paste state silver ultrafine particle dispersion liquid is 60 Pa-s.
[0047]the prepared paste state silver ultrafine particle dispersion liquid -- a printed-circuit board side top -- screen-stencil -- the print coating of circuit pattern shape -- it carried

out. To the coating film of this 50-micrometer thickness, it heat-treated by the temperature conditions for +210 **x 60 minutes under the inert atmosphere for 150 **x 30 minutes. The circuit wiring which sintering of the silver ultrafine particle contained in a coating film is made by this heat-treatment, and consists of a sintered compact film of the silver ultrafine particle formed as an alternative layer of a plating film on the surface of a printed-circuit board was formed. The resistance (rate of surface resistance) of the obtained circuit was $7.5x10^{-6}$omega and**.

[0048](Example 3) Paste state silver ultrafine particle dispersion liquid were prepared like Example 1. Per silver particulate 100 mass part with a mean particle diameter of 8 nm and as alkylamine, The dispersion liquid containing terpineol 75 mass part are used as dodecyl amine 15 mass part and an organic solvent, As an acid anhydride used as the ingredient which reacts to the dodecyl amine to contain per silver particulate 100 mass part in the dispersion liquid at the time of heating, methylhexahydrophthalic anhydride (Me-HHPA) 10 mass part was added, it fully stirred by stirring deaerator, and equalization was attained. The liquid viscosity of the prepared paste state silver ultrafine particle dispersion liquid is 60 Pa-s.

[0049]By screen-stencil, the prepared paste state silver ultrafine particle dispersion liquid were printed so that a through hole with an inside diameter of 0.5 mm of a double-sided wiring board with a substrate thickness of 1.6 mm might be embedded. To the coating film with a thickness [in this flat part] of 50 micrometers, it heat-treated by the temperature conditions for +210 **x 60 minutes under the inert atmosphere for 150 **x 30 minutes. By this heat-treatment, sintering of the silver ultrafine particle contained in a coating film was made, and the sintered compact film of the silver ultrafine particle formed in the internal surface of the through hole which penetrates a double-sided wiring board as an alternative layer of the plating film for through holes was formed. The resistance (connection resistance value between layers) of the conduction passage through the obtained through hole was per through hole and $9.1x10^{-6}$omega.

[0050]

[Effect of the Invention]In the formation method of a plating substitution conductive metal coat using the metal particulate dispersion liquid of this invention. As metal particles distributed in the metal particulate dispersion liquid to be used, use an ultra-fine particle with a mean particle diameter of 1-100 nm, and in the surface of the ultra-fine particle. Before spreading and printing controls condensation of this ultra-fine particle, and weld by providing a precise molecule enveloping layer with one or more sorts of compounds which have nitrogen, oxygen, and a basis containing a sulfur atom as a basis in which that metallic element and coordination combination are possible. In addition, a precise molecule enveloping layer also controls the natural oxidation on the surface of an ultra-fine particle, and also enables storage over the long period of time of this metal particulate dispersion liquid, and quality maintenance and maintenance of dispersion property. On the other hand in the organic solvent which is distributing the ultra-fine particle, At the temperature which heat-treats, removal of the enveloping layer of a compound which has a basis which includes the ultra-fine particle surface for a wrap, nitrogen, oxygen, and a sulfur atom by adding nitrogen, oxygen, the basis containing a sulfur atom, and the compound which has reactivity is enabled. The metal particles which hold the outstanding compressibility and moldability and are uniformly distributed in an organic solvent, Into a coating film, eventually, a precise filling state is taken, and it

touches mutually, and even if low temperature sintering is carried out and it compares the pure ultra-fine particle surface with a plating film while being heat-treated, an equal precise metallic film can form it with high reproducibility. In addition, unlike a common conductive metal paste, the paste state metal particulate dispersion liquid of this invention, Since sintering between ultra-fine particles attains the shape and conductivity excluding an organic binder component intrinsically, it does not depend on the shape of surface type of the portion applied, a crevice interval, etc., but makes it possible to give a homogeneous conductive film.